PATENT SPECIFICATION (11) 1 218 762

DRAWINGS ATTACHED

1 218 762

(21) Application No. 5377/68 (22) Filed 2 Feb. 1968

(45) Complete Specification published 13 Jan. 1971

(51) International Classification C01g 49/02 9/04 9/06

(52) Index at acceptance

C1A D10 D45 G39 G39D10 G39D45 N13A T8G1

(54) PROCESS FOR UTILIZATION OF SPENT PICKLE LIQUOR AND FLUE DUST

(71) I, LEONARD ANTHONY DUVAL, a citizen of the United States of America, of 207 Harmon Road, Aurora, State of Ohio, United States of America, do hereby declare

the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of removing zinc oxide from flue dust by treating the flue dust with spent pickle liquor.

Both flue dust and spent pickle liquor are normally considered to be serious industrial waste disposal problems.

In the past, many attempts have been made to dispose of flue dust or convert it to something of value, but the disposal of flue dust has remained a problem particularly to steel producers making steel by the basic oxygen process. Also, attempts have been made to solve the problem of what to do with spent pickle acid liquor and how to dispose of it without contaminating lakes or streams or how to economically convert the spent acid to something of value. In spite of these attempts the problem of disposing of the spent pickle acid liquor has remained and a great deal of time and money has been expended in trying to arrive at an answer to this problem.

The present invention provides a method which utilizes flue dust comprising zinc oxide and at least 50% by weight iron oxide and also spent pickle liquor derived from a pickling process using sulphuric or hydrochloric acid.

The present invention provides a method of removing zinc oxide from flue dust comprising zinc oxide and at least 50% by weight iron oxide, wherein the flue dust is treated with spent pickle liquor derived from a pickling process using hydrochloric or sulphuric acid at a temperature of 150° to 250°F. to at least partially leach the zinc oxide from the flue dust to form a zinc salt solution, followed by separation of the resultant leached flue dust from the zinc salt solution.

The flue dust may be collected from a basic steel producing process and the process of the invention renders such flue dust more suitable for re-use in an iron making process.

It is preferred that the spent pickle liquor initially has a pH of 3 to 5.5.

An analysis of a typical flue dust which can advantageously be processed by the process of the invention is as follows:

Ingredient	*Per cent by weight*
Iron	61 to 62
Sulphur	0.23
Zinc oxide	2.5 to 4.5
Water	10 to 15
Silica	2.4
Manganese	0.36
Phosphorus	0.4
Chromium	0.24
Other constituents	Balance

The flue dust processed preferably contains 0.25 to 4.0% by weight zinc oxide.

It has been found that when the treatment temperature is below 150°F., the leaching rate is so decreased that a greater treatment time is required than is economically feasible. It is preferred that the flue dust is reacted with the spent pickle liquor at 175° to 225°F. Generally, the flue dust is reacted with the spent pickle liquor at the boiling point of the liquor, the boiling point being determined by the composition of the spent pickle liquor.

When using a spent pickle liquor, derived from a pickling process using sulphuric acid, the initial sulphuric acid concentration of the liquor is preferably 0.5 to 6.0% by weight. When using spent pickle liquor derived from a pickling process using

hydrochloric acid, the initial hydrochloric acid concentration of the liquor is preferably 0.5 to 4.0% by weight.

After separating the resultant zinc salt solution from the leached flue dust (consisting predominantly of iron oxide), it is preferred to evaporate water from the solution to concentrate it or reduce it to dryness, and then to roast the resultant concentrated zinc salt solution or solid zinc salt to convert the iron salts therein to iron oxide and SO_3 gas or HCl gas (as the case may be) and to pass the gas through an absorption tower to recover sulphuric or hydrochloric acid.

Although atmospheric pressure is preferred, the treatment can be carried out under pressures both greater and lower than atmospheric.

It will be apparent to one skilled in the art that the pH of the resultant zinc salt solution, the composition of the resulting leached flue dust and the amount of zinc oxide leached from the flue dust depend on the relative initial quantities of the flue dust, the initial composition of the flue dust and the pickle liquor, and the temperature of treatment. However, these are matters of practical control.

It is preferred that the zinc salt solution is maintained at a pH of 1.0 to 5.5, more preferably 1.5 to 5.5 during the treatment of the flue dust. For commercial feasibility the pH should preferably be at least 3 because an effluent with a lower pH cannot be discarded properly in a sewer or stream. Furthermore, if the zinc salt solution has a pH lower than 3 it may be too corrosive to processing equipment used in recovering salt solutions. If the zinc salt solution has a pH of over 5.5 in the case of spent sulphuric acid pickle liquor or over 5 in the case of spent hydrochloric acid pickle liquor the treatment time is generally too long.

If the effluent has a pH of over 5.5, or over 5 in the case of spent HCl pickle liquor, which at the same concentration as H_2SO_4 will give a slightly lower pH, the resultant reaction time is generally much too long to reach the point of neutralization of the acid and conversion of the zinc oxide to zinc sulphate or zinc chloride.

Also, by keeping the pH of the zinc salt solution below 5.5, there is a minimum of conversion of the iron oxide of the flue dust to iron sulphate, $FeSO_4$. The conversion of iron to iron sulphate or iron chloride is undesirable inasmuch as it represents a loss of iron value for re-use as an oxide and the iron so converted necessitates recovery from its iron salt, either sulphate or chloride depending upon the acid used.

The accompanying drawing shows a flow sheet illustrating the removal of zinc oxide from flue dust according to the method of the invention.

As seen in the drawing, flue dust comprising zinc oxide and at least 50% by weight iron oxide is stored in a dust bin 3 from where it is moved by a blower 4 into a large dust storage tank 6 capable of holding 250 U.S. tons of dust. From the dust storage tank 6 the dust is continuously fed into one of a group of three reactors 10 where the flue dust is treated with spent pickle acid liquor. The spent pickle acid liquor derived from a pickling process using hydrochloric or sulphuric acid and is pumped to the reactor 10 from HCl liquor storage 12 or H_2SO_4 liquor storage 14, respectively.

In the reactor 10 the temperature is kept at 150°F. to 250°F. In the reactor 10 the spent pickle acid liquor reacts with the flue dust to leach the zinc oxide at least partially from the flue dust and a zinc salt solution is formed. The zinc salt is zinc chloride when the spent pickle liquor is derived from a process using hydrochloric acid. A leached flue dust slurry is formed in the reactor 10. From the reactor 10, the leached flue dust slurry and the zinc salt solution is passed to one of two thickeners 15 and then to one of filters 17. In the filter 17 the leached flue dust slurry and the zinc salt solution are filtered to provide a solid cake of leached flue dust. This cake typically contains about 65% by weight of iron and about 15% by weight of water. The filtrate from the filter 17 contains the zinc salt (zinc chloride or zinc sulphate), some iron salt (ferrous chloride or ferrous sulphate), unused acid (HCl or H_2SO_4) and water.

The filtrate is continuously fed into one of two evaporator units 20 where it is concentrated. The resultant concentrated filtrate is thereafter moved to one of two roasters 25 and roasted at about 270°F. to produce iron oxide by decomposition of the iron salt and HCl gas or SO_3 gas is continuously given off and passed through one of two gas absorption towers to either a sulphuric acid storage tank 28 or a hydrochloric acid storage tank 29. The zinc salts are not decomposed by this roasting.

As seen in the lower left-hand corner of the flow-sheet, the product from the roaster is mixed with water in one of washers 31 to form a slurry. The slurry is fed to one of thickeners 32 where it is concentrated by removal of zinc chloride or zinc sulphate in solution and the concentrated slurry is fed to one of filters 33 where it is filtered and the filtrate containing zinc chloride or sulphate in solution is passed to a zinc salt storage area which is a $ZnCl_2$ storage 34 or a $ZnSO_4$ storage 35. The zinc chloride or zinc sulphate in solution removed by the thickener 32 is also fed to the appropriate storage 34 or 35.

$ZnCl_2$ solution can be allowed to accumulate in storage 34 and $ZnSO_4$ solution can be allowed to accumulate in storage 35. The accumulation of $ZnCl_2$ or $ZnSO_4$ solution can be charged into the evaporator units 20 periodically, as for example at weekends, and the water removed therefrom to provide the solid zinc salt. The water removed from the zinc salt solution in the evaporator units 20 passes through condenser 37, where it is condensed and into a storage vessel 39. The resultant water in vessel 39 can be used in a manufacturing operation as it is clear and contains only a small amount of salts.

It has been found that it is highly desirable to thoroughly wash the filter cake from the filter 17, the filter cake before the washing comprising iron oxide particles. Each of the iron oxide particles apparently has a coating of zinc chloride or iron chloride clinging to it and this coating must be removed so that uncontaminated iron oxide can be produced for reuse in, for instance, iron making processes.

The following example illustrates that normal strength pickle liquor can be reduced to a pH level acceptable in many places for dumping into streams or lakes. By the liquor or effluent liquor is meant the zinc salt solution.

EXAMPLE

Two different flue dust samples were reacted with spent hydrochloric acid pickle liquor employing various reaction times and temperatures. Flue dust sample No. 1 contained approximately 63.1% by weight of iron and 0.8% by weight of zinc. Flue dust sample No. 2 contained approximately 63.3% iron and 0.78% zinc.

Results of said reactions are set forth below, the results including the percentage of iron and zinc remaining in the reacted dust and the pH of the resultant zinc salt solution:

Reaction No. 1 — 15 *Min.*, 180° *F*

	% *Fe*		% *Zn*		*pH Effluent Liquor*
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	61.7	0.8	0.5	
Dust No. 2	63.3	62.2	0.78	0.45	
Liquor	9.3	—			1

Reaction No. 2 — 30 *Min.*, 180° *F*

	% *Fe*		% *Zn*		*pH Effluent Liquor*
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	60.6	0.8	0.2	
Dust No. 2	63.3	61.1	0.78	0.18	
Liquor	9.3				Approx. 2

Reaction No. 3 — 45 *Min.*, 180° *F*

	% *Fe*		% *Zn*		*pH Effluent Liquor*
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	60.9	0.8	0.1	
Dust No. 2	63.3	60.7	0.78	None	
Liquor					4.5

Reaction No. 4 — 15 *Min.*, 200° *F*

	% *Fe*		% *Zn*		*pH Effluent Liquor*
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	62.7	0.8	0.46	
Dust No. 2	63.3	61.8	0.78	0.42	
Liquor	9.3		None	Trace	1

Reaction No. 5 — 30 *Min.*, 200° F

	% *Fe*		% *Zn*		*pH Effluent Liquor*
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	61.6	0.8	Trace	
Dust No. 2	63.3	61.2	0.78	0.01	
Liquor	10.1			Trace	2

Reaction No. 6 — 45 Min., 200° F

	% Fe		% Zn		pH Effluent Liquor
	Before	*After*	*Before*	*After*	
Dust No. 1	63.1	61.3	0.8	Trace	
Dust No. 2	63.3	60.9	0.78	0.01	
Liquor	10.4			0.01	4

It can be seen from the above data, that considerable amounts of zinc are removed from the flue dust samples by reaction under the above identified conditions of time and temperature.

Although reactions Nos. 1, 2, 4 and 5 removed substantial amounts of zinc, such reactions were not feasible from the standpoint of dumping the resultant zinc salt solution into a lake or stream, the pH being too acid for non-contaminating disposal.

WHAT I CLAIM IS:—

1. A method of removing zinc oxide from flue dust comprising zinc oxide and at least 50% by weight iron oxide, wherein the flue dust is treated at a temperature of 150°F. to 250°F. with spent pickle acid liquor derived from a pickling process using hydrochloric acid or sulphuric acid to at least partially leach the zinc oxide from the flue dust to form a zinc salt solution, followed by separation of the resultant leached flue dust from the zinc salt solution.

2. A method as claimed in claim 1, wherein the flue dust is collected from a basic steel producing process.

3. A method as claimed in either preceding claim, wherein a pH of 1 to 5.5 is maintained during the treatment of the flue dust.

4. A method as claimed in claim 3, wherein said pH is 3 to 5.5.

5. A method as claimed in any preceding claim, wherein the flue dust initially contains 0.25 to 4.0% by weight zinc oxide.

6. A method as claimed in any preceding claim, wherein the flue dust is treated, at a temperature of 175°F. to 225°F. with the spent pickle liquor.

7. A method as claimed in any preceding claim, wherein the flue dust is treated with the spent pickle liquor at the boiling point of the liquor.

8. A method as claimed in any preceding claim, wherein the spent pickle acid liquor is derived from a pickling process using sulphuric acid and the initial sulphuric acid concentration of the liquor is 0.5 to 6.0% by weight.

9. A method as claimed in any of claims 1 to 7, wherein the spent pickle liquor is derived from a pickling process using hydrochloric acid and the initial hydrochloric acid concentration of the liquor is 0.5 to 4.0% by weight.

10. A method as claimed in any preceding claim, wherein the treatment of the flue dust with the spent pickle liquor is carried out at atmospheric pressure.

11. A method as claimed in any preceding claim, wherein water is evaporated from the separated zinc salt solution to concentrate it or reduce it to dryness.

12. A method as claimed in claim 11, wherein the resultant concentrated zinc salt solution or solid zinc salt is roasted to convert any iron salts therein to iron oxide and HCl gas or SO_3 gas, and the gas is passed through an absorption tower to recover hydrochloric acid or sulphuric acid.

13. A method as claimed in claim 12, wherein the solid product of roasting is washed with water, the solid iron oxide and dissolved zinc salts are thereafter separated from one another, and water is evaporated from the zinc salt solution to concentrate it or reduce it to dryness.

14. A method as claimed in claim 1, and substantially as herein defined with reference to, and as illustrated in, the accompanying drawing.

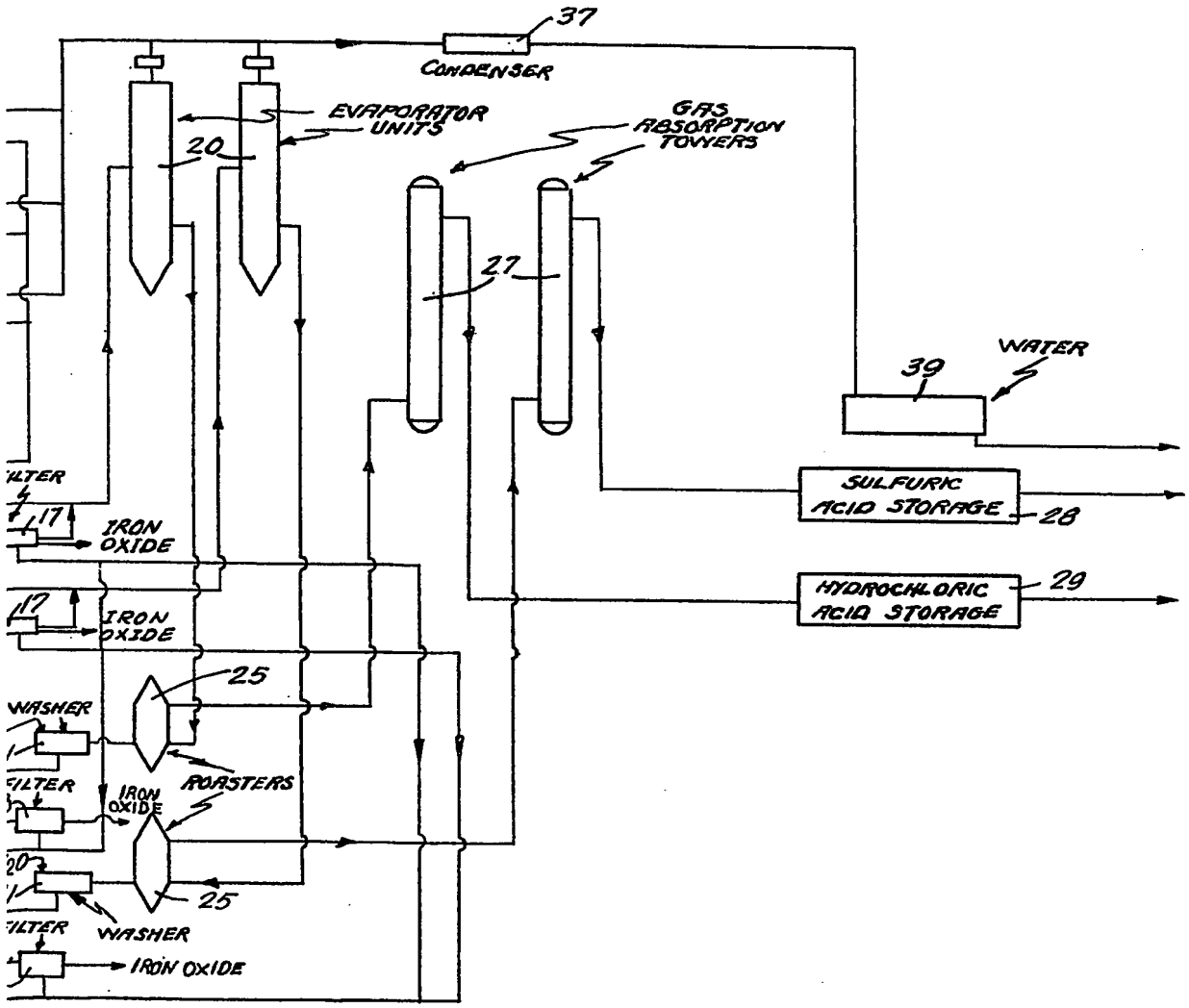
15. Flue dust treated by a method as claimed in any preceding claim.

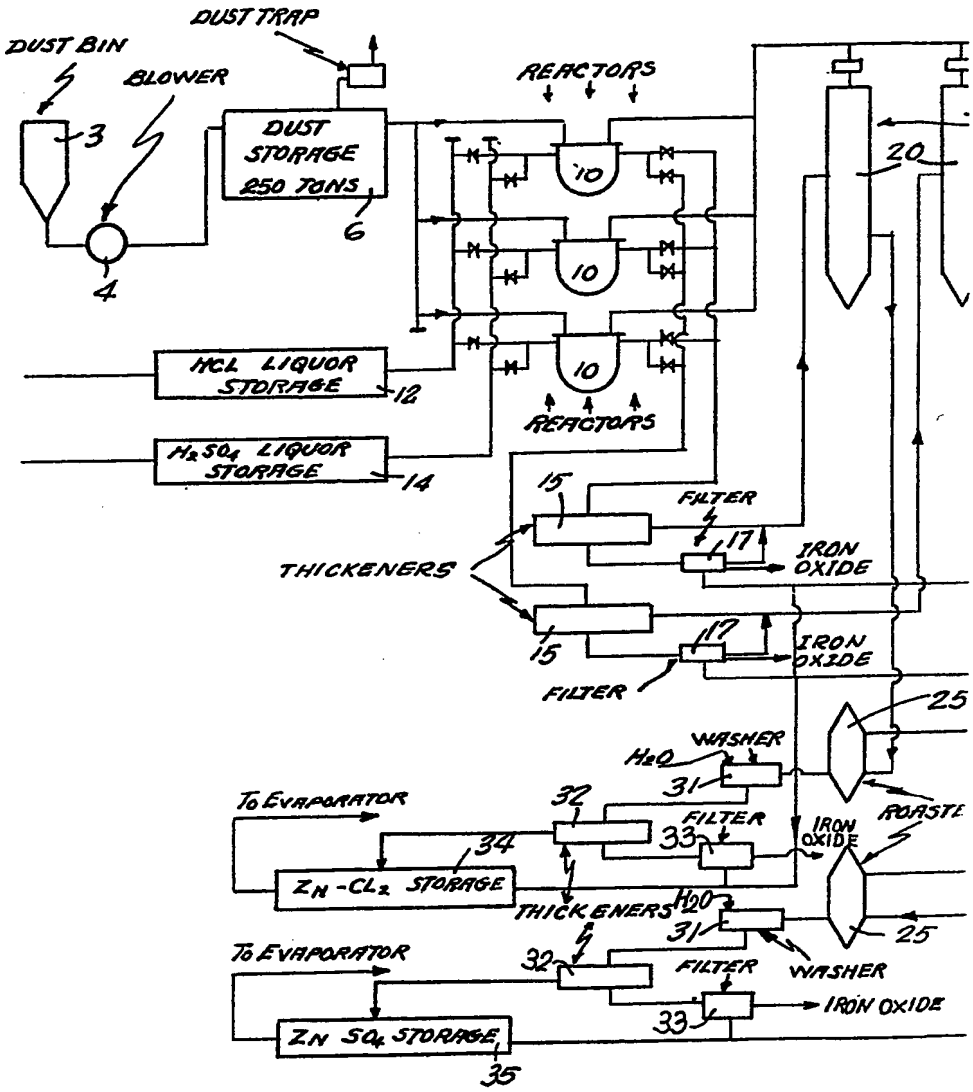
MARKS & CLERK.
Chartered Patent Agents.
Agents for the Applicant.

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1970
Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY from which copies may be obtained.

COMPLETE SPECIFICA

This drawing is a reproduc
the Original on a reduced




DUST TRAP
DUST BIN
BLOWER
REACTORS
DUST STORAGE 250 TONS
3
4
6
10
20
HCL LIQUOR STORAGE
12
H2SO4 LIQUOR STORAGE
14
REACTORS
15
FILTER
17
IRON OXIDE
THICKENERS
25
WASHER
H2O
31
32
FILTER
33
IRON OXIDE
ROASTE
TO EVAPORATOR
34
ZN-CL2 STORAGE
THICKENERS
H2O
31
25
TO EVAPORATOR
32
FILTER
WASHER
33
IRON OXIDE
ZN SO4 STORAGE
35

1,218,762
1 SHEET

COMPLETE SPECIFICATIO